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HIGH TEMPERATURE RESISTANT SALINE SOLUBLE FIBRES

This invention relates to high temperature resistant saline soluble fibres and particularly relates to calcium-magnesium-silicate fibres.

Calcium-magnesium-silicate fibres are known for example from WO89/12032, WO93/15028 and WO94/15883.

WO89/12032 first disclosed a broad class of fire-resistant saline soluble fibres.

WO93/15028 showed that a class of the fibres of WO89/12032 were usable at temperatures up to 1000°C or more.

WO94/15883 showed that some of the fibres of WO93/15028 had higher use temperatures still, of up to 1260°C or more, and indicated that such fibres needed a SiO₂ excess (defined as the amount of SiO₂ remaining after crystallisation of CaO, MgO and any ZrO₂ as silicates) of greater than 21.8mol%.

WO97/16386 while falling in the general class of calcium-magnesium-silicate fibres looked to low calcium fibres to show use temperatures of 1260°C or more.

It is apparent that there are regions of the CaO-MgO-SiO₂ and CaO-MgO-SiO₂-ZrO₂ composition fields within which high temperature performance fibres can be made and other regions where they cannot.

The applicants have now found a new and narrow range of compositions that are usable at temperatures of 1200°C or more and even 1250°C or 1260°C or more, and yet fall outside the scope of WO94/15883 and WO97/16386. These compositions preferably have little or no zirconia.

Accordingly the present invention provides a fibre having a maximum use temperature of 1200°C or more in which the amount of MgO in mol% is greater than the amount of CaO in mol % and which comprises:-

$\text{SiO}_2 > 64.25 \text{ wt\%}$

$\text{CaO} > 18 \text{ wt\%}$

$\text{MgO} < 17 \text{ wt\%}$.

However, no claim is made to fibres having a SiO_2 excess as specified of greater than 21.8mol%.

Further features of the invention are apparent from the appended claims.

The excess SiO_2 figure is calculated by treating all of the CaO as being bound as CaO.MgO.2SiO_2 ; all of the ZrO_2 as being bound as $\text{ZrO}_2.\text{SiO}_2$; and the remaining MgO as being bound as MgO.SiO_2 . The applicants also assume that any Al_2O_3 crystallises as $\text{Al}_2\text{O}_3.\text{SiO}_2$. Any remaining SiO_2 is called the excess SiO_2 .

The invention is illustrated by way of example in the following description with reference to the drawings in which

Fig 1 is a graph showing linear shrinkage with temperature for blankets comprising the fibres A4-2 and A4-3 of Table 1 below.

Fig. 2 is a graph showing shrinkage through the height of blankets comprising the fibres A4-2 and A4-3 of Table 1 below.

Fig. 3 is a graph showing shrinkage of preforms produced from fibres A4-1, A4-2 and A4-3 of Table 1 below.

Table 1 shows compositions extracted from WO89/12032, WO93/15028, WO94/15883, and WO97/16386 together with A4, a target composition fibre having the composition:-

SiO₂ 65 wt%

CaO 19.5 wt%

MgO 15.5 wt%

and A4-1, A4-2, and A4-3, which are analysed fibre samples.

The fibres extracted from the data of WO89/12032 (referred to as Manville fibres), WO93/15028, WO94/15883, and WO97/16386 (referred to as Unifrax fibres) are those for which the SiO₂ excess as specified is less than 21.8mol% and for which the amount of MgO in mol% is greater than the amount of CaO in mol%.

A4-1 was produced as bulk fibre; A4-2 was produced as needled blanket having a density of approximately 96 kg.m⁻³; and A4-3 was produced as needled blanket having a density of approximately 128 kg.m⁻³.

In Table 1 shrinkages are indicated from the documents concerned or, for A4-1, A4-2, and A4-3, from measuring the shrinkage of vacuum formed preforms of the fibres concerned.

Table I

Table 1															
Fibre	Shrinkage at 1260°C	Composition wt%							Composition mol%						SiO ₂ Excess
		CaO	MgO	ZrO ₂	Al ₂ O ₃	TiO ₂	SiO ₂	Others	CaO	MgO	ZrO ₂	Al ₂ O ₃	TiO ₂	SiO ₂	
924		19.78	14.54	0.66	2.57		61.32		19.99	20.44	0.30	1.43		57.84	15.68
SW-A1		20.50	15.20		1.10		63.70		20.16	20.79	0.00	0.59		58.46	16.92
B5	6.00	19.90	15.10	0.10	0.20		64.20	0.40	19.71	20.80	0.05	0.11		59.34	18.68
757		20.92	15.22	0.00	0.20		62.60		20.79	21.04	0.00	0.11		58.06	16.13
A4-1	1.86	20.20	15.50		0.26		64.60	0.07	19.76	21.10	0.00	0.14		59.00	18.00
A4-2	3.25	20.20	15.50		0.30		64.50	0.06	19.78	21.11	0.00	0.16		58.95	17.89
A4-3	2.76	20.20	15.60		0.28		64.70	0.07	19.72	21.18	0.00	0.15		58.95	17.9
A4 target		19.50	15.50				65.00		19.17	21.20	0.00	0.00		59.64	19.27
SW-A2		21.40	15.40		0.80		60.80		21.40	21.42	0.00	0.44		56.74	13.49
SW-A		20.50	15.50		3.30		59.30		20.66	21.73	0.00	1.83		55.78	11.56
932		21.60	15.65	0.11	1.50		59.85		21.58	21.75	0.05	0.82		55.80	11.60
Manville104		17.70	16.30		1.83		64.10		17.49	22.40	0.00	0.99	0.00	59.11	18.23
B9	5.00	18.10	17.10	0.10	0.20		64.40	0.20	17.72	23.29	0.04	0.11		58.84	17.69
971		23.92	17.36	0.05	0.74		56.82		23.56	23.79	0.02	0.40		52.23	4.47
B8	6.90	18.80	17.90	0.30	0.20		63.00	0.20	18.30	24.24	0.13	0.11		57.23	14.46
B16	4.30	15.10	18.10	0.30	0.10	0.10	66.00	0.20	14.78	24.65	0.13	0.05	0.07	60.31	20.69
A2-12		16.55	18.00	0.05	0.33		63.56		16.37	24.76	0.02	0.18		58.67	17.34
A2-30		16.06	18.21	0.00	0.40		63.68		15.89	25.07	0.00	0.22		58.82	17.64

Table 1

Table 1																
Fibre	Shrinkage at 1260°C	Composition wt%							Composition mol%							SiO ₂ Excess
		CaO	MgO	ZrO ₂	Al ₂ O ₃	TiO ₂	SiO ₂	Others	CaO	MgO	ZrO ₂	Al ₂ O ₃	TiO ₂	SiO ₂		
A2-23		18.59	18.78	0.05	0.48		60.20		18.37	25.82	0.02	0.26		55.53	11.06	
71		24.04	19.66	0.00	0.20		54.68		23.44	26.67	0.00	0.11		49.77	-0.45	
A2-19		18.48	19.74	0.00	0.54		58.71		18.29	27.18	0.00	0.29		54.24	8.47	
A2-21		13.74	19.98	0.13	0.34		64.16		13.51	27.34	0.06	0.18		58.90	17.81	
Unifrax comp 13	13.10	0.77	16.90	34.10	0.97		46.40		0.92	28.11	18.55	0.64		51.78	3.56	
A2-24		13.62	22.74	0.08	0.31		61.38		13.25	30.79	0.04	0.17		55.76	11.51	
Manville105		9.74	23.10		2.15		65.10		9.38	30.95	0.00	1.14	0.00	58.53	17.05	
Manville79		8.67	24.00		0.02		67.20		8.27	31.86	0.00	0.01	0.00	59.86	19.71	
A2-25		10.99	24.18	0.07	0.33		62.36		10.66	32.64	0.03	0.18		56.48	12.97	
Unifrax comp 14	23.40	0.89	21.70	24.10	0.90		51.90		0.98	33.18	12.05	0.54		53.24	6.49	
A2-35		8.88	24.88	0.47	0.29		64.12		8.56	33.37	0.21	0.15		57.71	15.41	
Manville78		6.43	26.50				67.10		6.07	34.80	0.00	0.00	0.00	59.13	18.25	
A2-34		6.63	26.20	0.80	0.23		64.85		6.37	35.01	0.35	0.12		58.15	16.29	
Unifrax comp 15	25.00	0.77	25.50	16.90	0.76		55.70		0.80	36.82	7.98	0.43		53.96	7.93	
Manville77		4.02	28.70		0.59		66.10		3.79	37.68	0.00	0.31	0.00	58.22	16.44	
Unifrax 42	2.00	0.30	29.75	0.58	0.62		68.63		0.28	38.92	0.25	0.32		60.23	20.47	

Table 1

Fibre	Shrinkage at 1260°C	Composition wt%								Composition mol%					SiO ₂ Excess
		CaO	MgO	ZrO ₂	Al ₂ O ₃	TiO ₂	SiO ₂	Others	CaO	MgO	ZrO ₂	Al ₂ O ₃	TiO ₂	SiO ₂	
Manville106		2.70	29.70		1.56		65.60		2.54	38.94	0.00	0.81	0.00	57.71	15.41
Manville80		1.60	30.10				68.40		1.49	39.02	0.00	0.00	0.00	59.49	18.98
Manville71		3.12	30.10		1.15		65.40		2.92	39.26	0.00	0.59	0.00	57.23	14.45
Manville76		3.12	30.10		1.15		65.40		2.92	39.26	0.00	0.59	0.00	57.23	14.45
Unifrax 47	7.70	0.25	30.26	0.01	1.86		67.53		0.23	39.56	0.00	0.96		59.24	18.48
Unifrax 40	9.20	0.27	30.57	0.58	0.92		67.52		0.25	39.90	0.25	0.47		59.13	18.25
765		3.90	35.07	0.00	2.12		57.78		3.62	45.26	0.00	1.08		50.04	0.07

It can be seen that the fibres according to the present invention show lower shrinkage at 1260°C than do the extracted fibres other than fibre Unifrax 42 which has a radically different composition.

In Figs. 1-3, graphs show the shrinkage characteristics of the fibres A4-1, A4-2, and A4-3 after 24 hours exposure to the indicated temperatures. it can be seen that the fibres are readily usable at temperatures of 1200°C or more.

Table 2 below shows the results of solubility tests on the fibres in physiological saline solution indicating that the fibres are soluble in body fluids. (See WO94/15883 for a discussion of methods of measuring solubility). Pairs of results are indicated for separate tests on each sample as is a mean total solubility.

Table 2					
Fibre type	Solubility (ppm)				
	CaO	MgO	SiO ₂	Total	Mean Total
A4-1	102	115	171	388	383
	105	110	162	377	
A4-2	105	116	172	393	395
	114	117	166	397	
A4-3	114	123	166	403	411
	114	128	177	419	

A typical range of compositions for fibres of the present invention would be

SiO₂ 65 ± 0.5 wt%

CaO 20 ± 0.5 wt%

MgO 15 ± 0.5 wt%.

Further tests were made on fibres having the inventive composition of SiO₂ 65%, CaO 19.5%, MgO 15.5% in comparison with Superwool 607™, a fibre having the nominal composition (by weight) of SiO₂ 65%, CaO 29.5%, MgO 5.5%, and Al₂O₃ <1% ; Superwool 612™, a fibre having the nominal composition (by weight) of SiO₂ 64.5%, CaO 17%, MgO 13.5%, ZrO₂ 5%; and refractory ceramic fibre having the nominal composition SiO₂ 56%, Al₂O₃ 44%.

The first test was aimed at indicating the amount of dust that might be released on handling. The test comprised the determination of the amount of dust present in a sample of blanket made from the respective fibres. The samples of blanket were vibrated on a Fritsch Analysette type 3010 vibratory sieve shaker, which was set for a frequency of 3000Hz and vertical amplitude of 0.5mm. The apparatus was equipped with a 1.6mm sieve and a pan. In the test method a sample of blanket 135mm x 135mm was placed on the sieve and vibrated for 10 minutes. The material collected in the pan was weighed and expressed as a percentage of the original weight of the sample. The results were as indicated below:-

<u>Fibre Material</u>	<u>Percent dust released</u>
Superwool 607™	0.16%
Inventive material	0.18%
Refractory ceramic fibre	0.25%
Superwool 612™	0.36%

From this it can be seen that the inventive fibre is of comparable low dustiness to Superwool 607™.

The second test made was to look to the shrinkage behaviour of blanket formed from the inventive fibre and the two Superwool™ fibres at high temperatures. Samples of blanket were exposed to specified temperatures for 24 hour periods and their linear shrinkage measured. The results are indicated in Table 3 below:-

	Table 3					
	Temperature					
Sample	1050°C	1110°C	1150°C	1200°C	1250°C	1300°C
Inventive fibre	0.8	0.6	1.0	1.0	1.5	4.2
Superwool 612™	0.7	1.0	1.1	1.7	1.8	12.1
Superwool 607™	0.4	0.4	0.5	0.6	4.8	7.8

This shows that the inventive fibre is comparable in performance with both Superwool™ fibres up to 1200°C. At 1250°C the Superwool 607™ fibre shows a shrinkage of 4.8% (which would be considered as too high a shrinkage for most applications). At 1300°C the inventive fibre while still showing a high shrinkage of 4.2% is the best of the three fibres tested.

A further series of tests were made to produce fibres on a production scale and the compositions of fibres obtained were as set out in Table 4 below. All showed low shrinkage at 1250°C (shrinkages were measured by different methods to Table 1 and are not directly comparable). In combination with the results of Table 1, this shows samples of usable characteristics having compositions consisting essentially of (in wt%):-

CaO 18.7 to 20.2

MgO 14.47 to 15.9

SiO₂ 64.5 to 65.1

Al₂O₃ 0 to 0.56

The fibres of the present invention therefore have a high solubility (desired to permit fibres to be cleared from the body quickly); a low dustiness (desired to reduce the amount of fibre that can be inhaled); and good high temperature characteristics.

Table 4																
Fibre	Linear shrinkage (%) at 1250°C	Composition wt%							Composition mol%						SiO ₂ Excess	
		CaO	MgO	ZrO ₂	Al ₂ O ₃	TiO ₂	SiO ₂	Others	CaO	MgO	ZrO ₂	Al ₂ O ₃	TiO ₂	SiO ₂		
SM	0.80	20.10	15.00		0.06		65.00		19.77	20.52	0.00	0.03		59.67	19.35	
TCI	0.78	18.90	15.50		0.38		65.10		18.63	21.26	0.00	0.21		59.90	19.81	
TCUK	no preform made	18.70	15.90		0.44		64.80		18.41	21.78	0.00	0.24		59.56	19.13	
TCUK2	2.6 (measured at 1300°C)	19.30	14.47		0.56	0.03	64.54	0.40	19.30	20.13	0.00	0.31		60.24	20.50	